

Leng *et al.* Reply: Conwell, Rothberg, and Mizes (CRM) claim [1] that, as a result of chain length distribution and vibronic sidebands of electronic levels in PPV films, there is little correlation between increase of pump photon energy ($\hbar\omega$) and increase of electronic energy, and therefore data from excitation spectroscopies such as those given in [2] cannot be used to study the electronic band structure of the polymers. Short chains and vibronic side band effects certainly broaden sharp spectroscopic features [3], but we disagree that these effects obscure spectroscopic data in "real samples." This can be demonstrated with a simple absorption spectrum $\alpha(\omega)$.

Figure 1 shows $\alpha(\omega)$ in a thin film of "standard" MEH-PPV up to 7 eV. In addition to the low energy excitonic band which peaks at 2.4 eV, there are three bands at 3.7, 4.7, and 5.9 eV, respectively (peaks II, III, and IV, respectively). These various absorption bands cannot be due to the lowest exciton of different PPV oligomers in the sample, because the lowest exciton level for $n = 3$ oligomer is at 3.2 eV [1], and we do not expect significant $n = 2$ or $n = 1$ contributions. We conclude that bands I to IV in Fig. 1(a) are due to *different electronic bands* in relatively long ($n \geq 7$) chains of MEH-PPV.

The various electronic absorption bands in Fig. 1(a) can

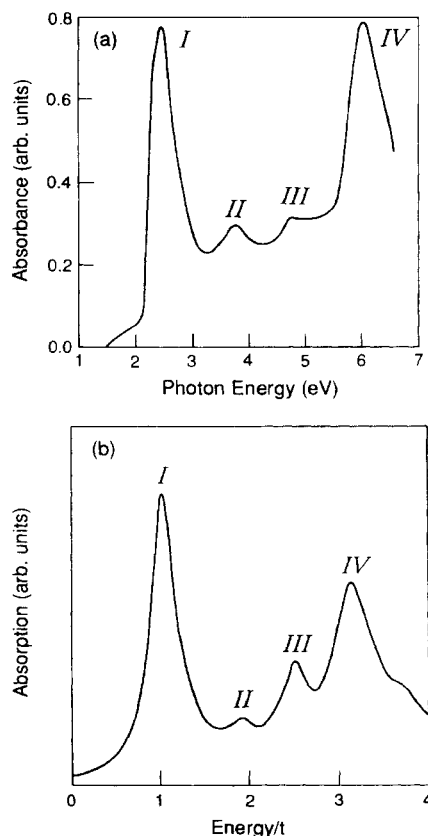


FIG. 1. (a) Absorption spectrum of a thin film of MEH-PPV. Bands I to IV are indicated. (b) Calculated absorption spectrum of an 8-unit PPV oligomer with a broadening parameter $\Gamma = 0.4$ eV; t is the transfer integral.

therefore be analyzed to obtain important information about the electronic band structure of MEH-PPV, including the location of the continuum threshold, by fitting $\alpha(\omega)$ against theoretical results. We have calculated $\alpha(\omega)$ of an 8-unit PPV oligomer within a theoretical model that is similar to the Pariser-Parr-Pople Hamiltonian [4], as shown in Fig. 1(b). The good agreement between the experimental and calculated $\alpha(\omega)$ reconfirms that bands I to IV are indeed different electronic absorptions in MEH-PPV. From our model we found the continuum threshold to be at 3.1 eV [4], in agreement with our original assignment [2].

We note that in addition to short chains, standard PPV samples are also subject to disorder caused by cross-links, impurities, and defects. These give rise to a distribution of shallow traps, which are best revealed in $\alpha(\omega)$ as an absorption tail below the absorption edge [Fig. 1(a)]. The interaction of photogenerated excitons with these shallow traps may alter their radiative transition probability to such an extent that the correlation between $PA(t)$ and $PL(t)$, in transient optical measurements, no longer holds. Under these conditions, the fact that $PL(t)$ decays faster than $PA(t)$ [2] does not necessarily show that they come from different species, as claimed by CRM in [1].

The pump $\hbar\omega$ in our original picosecond transient measurements was 2.17 eV, which is in the absorption tail of PPV [2]. Therefore, the excitons were directly generated into localized states, since $\hbar\omega < E(1B_u)$ (≈ 2.4 eV) in long PPV chains [1]. Under these conditions the photogenerated excitons do not have the necessary excess energy to dissociate into polaron pairs. We thus maintain that *excitons* give rise to the PA band at 1.75 eV that we originally observed in [2].

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